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D. Barmes

Telephone No.: (41-22) 730.91.11

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Authorised officer:

B. Fitzgerald

Facsimile No.: (41-22) 740.14.35

Telephone No.: (41-22) 730.91.11

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(71) Applicant (for all designated States except US): TECHNOLOGICAL RESOURCES PTY. LIMITED [AU/AU]; A.C.N. 002 1833 557, Level 39, 55 Collins Street, Melbourne, VIC 3001 (AU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HOLLITT, Michael, John [AU/AU]; 80 Tyne Street, Box Hill North, VIC 3129 (AU). McCLELLAND, Ross, Alexander [AU/AU]; Lot 136 Murrawong Road, Maryknoll, VIC 3812 (AU). TUFFLEY, John, Roger [AU/AU]; 15 Hill Street, Burnside, S.A. 5066 (AU).

(74) Agent: BLAIR, J., G.; Griffith Hack & Co., 3rd Floor, 509 St. Kilda Road, Melbourne, VIC 3004 (AU).

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(54) Title: UPGRADING TITANIFEROUS MATERIALS

(57) Abstract

The application discloses a process for upgrading a titaniferous material by removal of impurities contained in the material especially radionuclides. The process involves heating the titaniferous material to a temperature of less than 1300 °C to form a solid titaniferous phase and a liquid oxide or glassy phase in the presence of a material that promotes the formations of such phases, cooling the product at a rate that maintains the glassy phase in an amorphous state and leaching the solidified material with an acid or an alkali to remove the impurities. Materials that promote the formation of the desired phases include compounds of alkali metals and boron. Examples include borax, caustic soda, soda ash and silica.

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UPGRADING TITANIFEROUS MATERIALS

This invention relates to the removal of impurities from naturally occurring and synthetic titaniferous materials.

5 The invention is particularly suited to the enhancement of titaniferous materials used in the production of titanium metal and titanium dioxide pigments by means of industrial chlorination systems.

10

Embodiments of the present invention have the common feature of roasting of titaniferous materials in the presence of additives and at temperatures which encourage the formation of a liquid oxide or glassy phase, followed at some stage by
15 cooling and aqueous leaching as steps in an integrated process. Additional steps may be employed as will be described below.

20 In industrial chlorination processes titanium dioxide bearing feedstocks are fed with coke to chlorinators of various designs (fluidised bed, shaft, molten salt), operated to a maximum temperature in the range 700 - 1200C. The most common type of industrial chlorinator is of the fluidised bed
25 design. Gaseous chlorine is passed through the titania and carbon bearing charge, converting titanium dioxide to titanium tetrachloride gas, which is then removed in the exit gas stream and condensed to liquid titanium tetrachloride for further purification and processing.

30

The chlorination process as conducted in industrial chlorinators is well suited to the conversion of pure titanium dioxide feedstocks to titanium tetrachloride. However, most other inputs (i.e. impurities in feedstocks) cause difficulties which greatly complicate either the chlorination process itself or the subsequent stages of condensation and purification and disposal of waste. The attached table provides an indication of the types of problems encountered. In addition, each unit of inputs which does not enter products contributes substantially to the generation of wastes for treatment and disposal. Some inputs (e.g. particular metals, radioactives) result in waste classifications which may require specialist disposal in monitored repositories.

Preferred inputs to chlorination are therefore high grade materials, with the mineral rutile (at 95-96% TiO_2) the most suitable of present feeds. Shortages of rutile have led to the development of other feedstocks formed by upgrading naturally occurring ilmenite (at 40-60% TiO_2), such as titaniferous slag (approximately 86% TiO_2) and synthetic rutile (variously 92-95% TiO_2). These upgrading processes have had iron removal as a primary focus, but have extended to removal of magnesium, manganese and alkali earth impurities, as well as some aluminium.

	Elemental Input	Chlorination	Condensation	Purification
5	Fe, Mn	Consumes chlorine, coke, increases gas volumes	Solid/liquid chlorides foul ductwork, make sludges	
10	Alkali & alkali earth metals	Defluidise fluid beds due to liquid chlorides, consume chlorine, coke		
15				
20	Al	Consumes chlorine, coke	Causes corrosion	Causes corrosion, makes sludges
25	Si	Accumulates in chlorinator, reducing campaign life.	Can encourage duct blockage. Condenses in part with	May require distillation from product
30		Consumes coke, chlorine	titanium tetrachloride	
35	V			Must be removed, by chemical treatment and distillation
40	Th, Ra	Accumulates in chlorinator brickwork, radioactive; causes disposal difficulties		
45				

In the prior art synthetic rutile has been formed from titaniferous minerals, e.g. ilmenite, via various techniques. According to the most commonly applied technique, as variously operated in Western Australia, the titaniferous

mineral is reduced with coal or char in a rotary kiln, at temperatures in excess of 1100 C. In this process the iron content of the mineral is substantially metallised. Sulphur additions are also made to convert manganese impurities partially to sulphides. Following reduction the metallised product is cooled, separated from associated char, and then subjected to aqueous aeration for removal of virtually all contained metallic iron as a separable fine iron oxide. The titaniferous product of separation is treated with 2-5% aqueous sulphuric acid for dissolution of manganese and some residual iron. There is no substantial chemical removal of alkali metals or alkaline earths, aluminium, silicon, vanadium or radionuclides in this process as disclosed or operated. Further, iron and manganese removal is incomplete.

Recent disclosures have provided a process which operates reduction at lower temperatures and provides for hydrochloric acid leaching after the aqueous aeration and iron oxide separation steps. According to these disclosures the process is effective in removing iron, manganese, alkali and alkaline earth impurities, a substantial proportion of aluminium inputs and some vanadium as well as thorium. The process may be operated as a retrofit on existing kiln based installations. However, the process is ineffective in full vanadium removal and has little chemical impact on silicon.

In another prior art invention relatively high degrees of removal of magnesium, manganese, iron and aluminium have been achieved. In one such process ilmenite is first thermally reduced to substantially complete reduction of its ferric oxide content (i.e. without substantial metallisation), normally in a rotary kiln. The cooled, reduced product is then leached under 35 psi pressure at 140-150 C with excess 20% hydrochloric acid for removal of iron, magnesium,

aluminium and manganese. The leach liquors are spray roasted for regeneration of hydrogen chloride, which is recirculated to the leaching step.

5 In other processes the ilmenite undergoes grain refinement by thermal oxidation followed by thermal reduction (either in a fluidised bed or a rotary kiln). The cooled, reduced product is then subjected to atmospheric leaching with excess
10 20% hydrochloric acid, for removal of the deleterious impurities. Acid regeneration is also performed by spray roasting in this process.

In all of the above mentioned hydrochloric acid leaching based processes impurity removal is similar. Vanadium,
15 aluminium and silicon removal is not fully effective.

In yet another process ilmenite is thermally reduced (without metallisation) with carbon in a rotary kiln, followed by cooling in a non-oxidising atmosphere. The cooled, reduced
20 product is leached under 20 - 30 psi gauge pressure at 130°C with 10 - 60% (typically 18 - 25%) sulphuric acid, in the presence of a seed material which assists hydrolysis of dissolved titania, and consequently assists leaching of
25 impurities. Hydrochloric acid usage in place of sulphuric acid has been claimed for this process. Under such circumstances similar impurity removal to that achieved with other hydrochloric acid based systems is to be expected. Where sulphuric acid is used radioactivity removal will not be complete.

30

A commonly adopted method for upgrading of ilmenite to higher grade products is to smelt ilmenite at temperatures in excess of 1500°C with coke addition in an electric furnace, producing a molten titaniferous slag (for casting and

crushing) and a pig iron product. Of the problem impurities only iron is removed in this manner, and then only incompletely as a result of compositional limitations of the process.

5

10 In another process titaniferous ore is roasted with alkali metal compounds, followed by leaching with a strong acid other than sulphuric acid (Australian Patent No. AU-B-70976/87). According to this disclosure substantial removal of various impurities is achieved, with "substantial" defined to mean greater than 10%. In the context of the present invention such poor removal of impurities, especially of thorium and uranium, would not represent an effective process. No specific phase structure after roasting is
15 indicated for this process but it is evident from analytical results provided (where product analyses, unlike feed analyses do not sum to 100% and analyses for the alkali metal added are not given) that there may have been significant retention of the additive in the final product. Under the
20 conditions given it is herein disclosed that it is to be expected that alkali ferric titanate compounds which are not amenable to subsequent acid leaching will form. The consequent retention of alkali will render the final product unsuitable as a feedstock for the chloride pigment process.

25

In yet another process a titaniferous ore is treated by alternate leaching with an aqueous solution of alkali metal compound and an aqueous solution of a mineral acid (US Patent No. 5,085,837). The process is specifically limited to ores
30 and concentrates and does not contemplate prior processing aimed at artificially altering phase structures. Consequently the process requires the application of excessive reagent and harsh processing conditions to be even partially effective and is unlikely to be economically

implemented to produce a feedstock for the chloride pigment process.

5 A wide range of potential feedstocks is available for upgrading to high titania content materials suited to chlorination. Examples of primary titania sources which cannot be satisfactorily upgraded by prior art processes for the purposes of production of a material suited to chlorination include hard rock (non detrital) ilmenites,
10 siliceous leucoxenes, many primary (unweathered) ilmenites and large anatase resources. Many such secondary sources (e.g. titania bearing slags) also exist.

Clearly there is a considerable incentive to discover methods
15 for upgrading of titaniferous materials which can economically produce high grade products almost irrespectively of the nature of the impurities in the feed.

The present invention provides a combination of processing
20 steps which may be incorporated into more general processes for the upgrading of titaniferous materials, rendering such processes applicable to the treatment of a wider range of feeds and producing higher quality products than would otherwise be achievable.

25

Accordingly, the present invention provides a process for upgrading a titaniferous material by removal of impurities which process includes the steps of:-

(i) heating a titaniferous material to a
30 temperature less than 1300°C to produce a solid titaniferous phase and a liquid oxide or glassy phase in the presence of sufficient of compounds which encourage the formation of the liquid oxide or glassy phase;

5 (ii) cooling the product of step (i) to form a solidified material comprising the titaniferous phase and an impurity bearing phase at a rate sufficient to ensure the susceptibility of the impurity bearing phase to leaching in either an acid or alkaline leachant; and

10 (iii) leaching the solidified material in an acidic or alkaline leachant to leach at least a portion of the impurities.

15 In order to ensure the formation of the solid titaniferous phase and the liquid oxide or glassy phase during the heating step it will normally be necessary to add to the titaniferous material, prior to the heating step, sufficient of a compound that encourages the formation of the liquid oxide or glassy phase. However, in some cases it will not be necessary since the titaniferous material itself may contain sufficient of
20 such a compound.

25 It has been discovered that the process of the invention can remove iron, magnesium and other alkaline earths, alkalis, manganese, silica, phosphorus, alumina, vanadium, rare earths, thorium and other radioactive elements, which impurities form an almost comprehensive list of impurities in titaniferous mineral sources. From most materials a product purity of greater than 96% TiO_2 can be obtained.

30 Compounds added to the titaniferous material may be mixed therewith by any means ranging from direct mixing of additives prior to charging to thermal treatment to more complex feed preparations such as the formation of agglomerates or nodules of mixed products, to briquette

production from feeds and additives. Many additives will be effective. In particular it is herein disclosed that sodium, potassium, lithium, phosphorus, silicon and boron compounds and minerals (e.g. borax, trona and other alkali metal carbonates, spodumene, caustic soda) will be effective. Additives may be incorporated individually or in combination with other additives.

It is further disclosed herein that the formation of a glassy phase by addition of alkali compounds can be achieved without the formation of alkali titanate phases, reduced alkali titanate phases (e.g. NaTiO_2 - compounds and solid solutions) or alkali ferric titanate phases (e.g. Na(Fe, Al)O_2 - TiO_2 phases known as "bronzes") in roasting. Where such titanate phases form their stability with respect to subsequent leaching steps is such that the final product quality is adversely affected. The incorporation of sufficient quantities of further additives (e.g. boron or phosphorus compounds) which substantially reduce alkali oxide chemical activity can have the effect of eliminating these phases.

Under many circumstances it will be beneficial to incorporate multiple additives into the material to be treated by thermal processing. For example, it is herein disclosed that the simultaneous presence of silica, anhydrous borax and sodium oxide in 1000°C thermally processed material in weight ratios of about 7:1:1 ensures the preferential formation of a glassy phase over other phases containing silica or soda. In this formulation the required borax addition is only just over 10% of the addition which would be required for an equivalent amount of glassy phase where other additives do not act as extenders. Since borax is by far the most expensive additive of the three additives in this case optimum economics are achieved by the use of the extenders.

Thermal processing may be carried out in any suitable device. The production of liquid phases would recommend rotary or grate kilning, but shaft furnaces may also be used and it has
5 been found that fluidised beds can be used under some circumstances. Any gaseous atmosphere conditions may be used, from fully oxidising to strongly reducing. The thermal processing atmosphere should be chosen to most suit other steps in integrated processing. Reducing conditions may be
10 achieved where desired by either the use of a sub stoichiometric firing flame or the addition of coal, char or coke with the thermal processing charge.

Thermal processing residence time at temperature will depend
15 on the nature of the additives and the feed, as well as the operating temperature. Residence times of from 5 minutes to five hours have been effective, allowing thermal processing residence times to be set to most suit other requirements in integrated processing.

20 The level of additive used and the conditions applied in thermal processing should be such that glassy phase formation does not exceed the limitations set by materials handling constraints in the thermal processing step. For example,
25 where glassy phase formation exceeds about 15% by volume of the roasted material it must be anticipated that accretion and bed fusion problems will occur.

Cooling of the thermally treated material should be conducted
30 in such a manner as to limit the reversion of the glassy phase to crystalline phases, i.e. should be at a sufficient rate to a temperature at which the liquid glass solidifies as to ensure the formation of at least a portion of solid glass rather than complete formation of crystalline products.

Further, cooling should be conducted under an environment appropriate to the conditions of thermal treatment (i.e. reduction processing will require cooling in an oxygen free environment).

5

The aqueous leaching step need not necessarily follow directly after the presently disclosed thermal processing step. For example if the thermal processing step is conducted under oxidising conditions it may be optionally followed by a reduction step prior to aqueous leaching. Further, crushing/grinding of the thermally processed material to enhance subsequent leach performance may be undertaken.

10

The conditions necessary to conduct effective leaching will depend on the nature of the original feed and the additives. For example, addition of soda ash and borax to siliceous leucoxene in accordance with the present disclosure will result in a product which can be leached in sodium silicate solution formed directly from the thermally treated material; the active leachant in this case is simply water. In other cases up to 100 g/L caustic soda solution or acid will be an effective leachant. Leaching will generally benefit substantially by use of high temperature (e.g. 80°C or above), although it has not been necessary to use pressure leaching to achieve effective conditions. Nevertheless it is presently disclosed that pressure leaching can be effectively and successfully applied. Lower temperatures can also be used, although with penalties in process kinetics.

15

20

25

Leaching may be conducted in any circuit configuration, including batch single or multiple stage leaching, continuous cocurrent multistage leaching, or continuous countercurrent multistage leaching. For most circumstances two stage cocurrent leaching will be most beneficial. Average residence

30

time may vary from 30 minutes to 10 hours, depending on process conditions. Any leach vessel capable of providing adequate shear may be used. Simple stirred tank vessels are applicable.

5

At the conclusion of leaching the leach liquor may be separated from the mineral by any suitable means, including thickening, filtration and washing. The mineral product may then pass on to other steps in an integrated process. For example, a further acid leach may follow the disclosed leaching step, particularly where the titaniferous feed has a content of alkalis or alkaline earths.

10

Other processing steps may be added as necessary or desired. For example, reagent regeneration (e.g. caustic regeneration, hydrochloric acid regeneration, sulphuric acid regeneration) can be used with the process in order to improve process effectiveness or economics. Similarly, a physical separation step may be employed at any stage (e.g. a final magnetic separation to remove grains containing iron, such as chromite).

20

Examples

Example 1

25 Sodium carbonate addition, corresponding to 4.25% Na_2O by weight, was made to a titania concentrate whose composition is given in Table 1. The mixture was homogenised and pelletised, and the pellets were heated in air to 1000°C for 4 hours. The thus roasted pellets were quenched in liquid
30 nitrogen and then crushed to pass a screen of 200 microns aperture. The crushed roasted pellets were subjected to leaching under reflux with 40 wt% sodium silicate solution ($\text{SiO}_2:\text{Na}_2\text{O}=2,4:1$ by weight) at 4% slurry density. (Sodium silicate solution was used to simulate leaching using water

as leachant under conditions where the leach liquors are recycled to leaching after solid/liquid separation).

5 Solid/liquid separation was effected by centrifuging, after which the leach residue was washed and calcined at 1000°C for analysis. The analysis of the calcined product is also given in Table 1.

10 The original concentrate was known to contain silica primarily as quartz inclusions in titanate grains. X-ray diffraction analysis after roasting indicated extinction of all crystalline phases containing silica. A glassy phase containing 16% Na₂O, 46% SiO₂, 9% Al₂O₃, 26% TiO₂ and 3% Fe₂O₃ was identified in the roasted material by electron
15 microscopy. Sodium titanates and sodium iron titanium bronze were also identified (along with rutile) by these techniques, indicating that conditions were not optimised.

20 Nevertheless, highly effective concentrate upgrading has been achieved even where the benefits of subsequent acid leaching have not been pursued, illustrating the benefits of the formation of the glassy phase. Substantial removal of silica, alumina and vanadium was achieved.

25 Example 2

This example illustrates the optimisation of additives for both process effectiveness and most economic formulation.

30 In this example titania concentrates of the composition given in Table 2 were used as titaniferous material for treatment. Early work attempting to produce glassy phase with this material by addition of sodium carbonate prior to roasting indicated that glassy phase could easily be produced, but over a wide range of conditions reduced sodium titanate or

sodium iron titanate bronze formation which resulted in sodium retention after leaching could not be easily avoided.

5 Complete and partial replacement of sodium carbonate by borax was tested.

Two batches of hand pressed pellets were prepared as follows. A 100g sample of the concentrates (previously ground to passing a screen aperture of 30 microns) was blended in each case with 1.1% of the appropriate additive or additive mixture and the resulting blends were pressed into pellets. The first batch was prepared with 1.1 wt% of anhydrous borax addition while the second batch was prepared with addition of 1.1 wt% of 1 : 1 $\text{Na}_2\text{B}_4\text{O}_7:\text{Na}_2\text{O}$.

15 Each batch of pellets was roasted for two hours in a 7 : 1 H_2/CO , atmosphere at 1000°C and then removed to cool quickly in the same atmosphere. The roasted pellets were ground to pass a screen aperture of 75 microns for subsequent leaching. 20 Ground roasted pellets were caustic leached under reflux conditions for 6 hours in a 10% NaOH solution at 6.7% solids density. Solid/liquid separation was effected by filtration, and the caustic leached products were washed and dried in preparation for subsequent acid leaching.

25 The caustic leached residues were acid leached in 15% HCl for 4 hours under reflux, then similarly filtered, washed and dried.

30 In each case samples of the concentrate and roasted material were submitted for X-ray diffraction analysis. While quartz and various ilmenite, anatase and rutile related phases were identified in the concentrates the only crystalline phases identified in the roasted product were rutile and ilmenite.

All quartz had entered a glassy phase, and no titanate phases which would reduce leach effectiveness were identified.

Analyses of the caustic and acid leach residues in each case, illustrating the effectiveness of the process where optimum conditions are applied, are provided in Table 3.

Example 3

The same pellet formulations as indicated in Example 2 were made up in 350 kg batches in an agglomeration plant and roasted at 30 kg/hr feed rate with 15% brown coal char addition to a final temperature of 1000°C in a small (0.5m diameter) rotary kiln. Residence time above 900°C was approximately 10 minutes. There were no problems with accretions or bed fusion, and after separation from residual char the products had exactly the same properties as the roasted products of Example 2.

Example 4

A commercial titania slag product having the composition indicated in Table 4 was processed as for the processing conditions indicated in Example 2, but with 2 wt% anhydrous borax addition in place of the other additives. The caustic leach was conducted at 165°C under pressure, and a pressure leach with 20% sulphuric acid conducted at 135°C was used in place of the hydrochloric acid leach. The final residue was calcined at 900°C for one hour. The products of this treatment are indicated in Table 4.

Example 5

This example when compared with examples 1 and 2 illustrates the advantages of the formation of a glassy phase.

Concentrates having the composition indicated in Table 1 were

subjected leaching under atmospheric reflux conditions with excess 20% HCl. After separation of the residue from the liquor followed by washing and drying of the residue its composition was as given in Table 5. Clearly there was ineffective removal of virtually all impurities of interest by comparison with the other examples provided herein.

Table 1: Concentrates and Product from Example 1

wt%	Concentrate	Product
10	TiO ₂	85.8
	Fe ₂ O ₃	2.25
	Al ₂ O ₃	1.08
	SiO ₂	7.62
	Nb ₂ O ₅	0.30
15	V ₂ O ₅	0.235
	Na ₂ O	0.0
		1.10

Table 2: Composition of Concentrates
Used in Examples 2 and 3

	wt%
20	TiO ₂
	63.6
	Fe ₂ O ₃
	28.6
	SiO ₂
25	3.53
	Al ₂ O ₃
	0.80
	MgO
	0.87
	CaO
	0.02
	Cr ₂ O ₃
	0.55
	MnO
30	1.11
	V ₂ O ₅
	0.22
	ZrO ₂
	0.26
	P ₂ O ₅
	0.04
	U ₃ O ₈
	0.002
	ThO ₂
	0.01

Table 3: Compositions of Leach Products from Example 2

5	wt%	1.1% Na ₂ B ₄ O ₇ addition		1.1% 1:1 Na ₂ B ₄ O ₇ :Na ₂ O addition	
		Caustic Leach Residue	Acid Leach Residue	Caustic Leach Residue	Acid Leach Residue
10	TiO ₂	66.9	94.3	67.3	94.9
	Fe ₂ O ₃	27.1	30.2	30.6	2.04
	SiO ₂	1.12	0.99	0.55	0.86
	Al ₂ O ₃	0.22	0.17	0.14	0.15
	MgO	0.97	0.08	0.90	0.09
15	CaO	0.05	0.001	0.03	0.001
	Cr ₂ O ₃	0.68	0.69	0.70	0.67
	MnO	1.15	0.06	1.19	0.06
	V ₂ O ₅	0.22	0.15	0.23	0.13
	ZrO ₂	0.27	0.37	0.28	0.38
20	Na ₂ O	0.05	0.02	0.15	0.03
	P ₂ O ₅	0.02	0.02	0.01	0.02
	U ₃ O ₈	0.002	0.002	0.002	0.002
	ThO ₂	0.01	0.003	0.01	0.004

Table 4: Feed and Product in Example 4

	wt%	Commercial Slag	Roast/Leach Product
5	TiO ₂	79.7	97.2
	FeO	9.24	0.85
	SiO ₂	3.11	0.09
	Al ₂ O ₃	3.23	0.38
	MgO	4.81	0.43
10	CaO	0.41	0.002
	Cr ₂ O ₃	0.16	0.12
	MnO	0.25	0.02
	V ₂ O ₅	0.57	0.12
	ZrO ₂	0.046	0.06
15	P ₂ O ₅	0.002	0.004
	U ₃ O ₈	0.0005	n.d.
	ThO ₂	0.0006	n.d.

n.d. = not determined

20

Table 5: Results of Processing as described in Example 5

	wt%	Leach Product
	TiO ₂	88.6
25	Fe ₂ O ₃	0.98
	SiO ₂	7.54
	Al ₂ O ₃	0.65
	V ₂ O ₅	0.198
	U ₃ O ₈	0.0054
30	ThO ₂	0.0094

CLAIMS

1. A process for upgrading a titaniferous material by removal of impurities which process includes the steps of:-

- 5 (i) heating a titaniferous material to a temperature of less than 1300°C to produce a solid titaniferous phase and a liquid oxide or glassy phase in the presence of sufficient of compounds which encourage the formation of the liquid oxide or glassy phase;
- 10 (ii) cooling the product of step (i) to form a solidified material comprising the titaniferous phase and an impurity bearing phase at a rate sufficient to ensure the susceptibility of the impurity bearing phase to leaching in either an acid or alkaline leachant; and
- 15 (iii) leaching the solidified material with an acidic or alkaline leachant to leach at least a portion of the impurities.
- 20

2. A process for upgrading a titaniferous material according to Claim 1 wherein the compounds which encourage the formation of the liquid oxide or glassy phase at a temperature below 1300°C are compounds of sodium, potassium, lithium, phosphorus silicon or boron.

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3. A process for upgrading a titaniferous mineral according to Claim 2, wherein the compound of sodium is caustic soda.

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4. A process for upgrading a titaniferous mineral according to Claim 2, wherein the compound of sodium is sodium carbonate.

5. A process for upgrading a titaniferous mineral according to Claim 2, wherein the compounds include borax.
- 5 6. A process for upgrading a titaniferous mineral according to Claim 2, wherein the compounds comprise a mixture of soda ash and borax.
- 10 7. A process according to Claim 6, wherein the titaniferous material is heated to a maximum temperature of 1000°C for a period which avoids substantial reduction to metal of contained iron oxides.
- 15 8. A process according to Claim 7, wherein the solidified material is leached with water.
- 20 9. A process according to Claim 7, wherein the solidified material is leached with a recycled solution of leach liquor containing sodium silicate and borax to form a leachate and a residue.
- 25 10. A process according to Claim 9, wherein the leachate is separated from the residue and the residue is leached with hydrochloric acid having an acid strength in a range from 1 to 20% hydrochloric acid.
- 30 11. A process according to claim 1 wherein the compounds include compounds which extend the effect of other compounds.
12. A process according to claim 11 wherein a compound which extends the effect of other compounds is borax.
13. A process according to claim 1 wherein sufficient compounds are present to avoid the formation of titanate

phases that are not amenable to subsequent leaching.

14. A process according to claim 1 wherein the solidified material is leached under mild conditions.

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15. A process according to claim 14 wherein the solidified material is leached at atmospheric pressure.

16. An upgraded titaniferous material produced by the process of any one of claims 1 to 15.


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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 93/00414

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ C22B 1/00, 1/02 // C22B 34/12					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols) IPC : C22B 1/00, 1/02, 34/12, 53/00					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above					
Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.			
X	AU,A, 70976/87 (E.I. DU PONT DE NEMOURS & CO) 8 October 1987 (08.10.87) Page 2 line 25 - page 3 line 10, page 8 line 7 - page 10 line 13	1-4,13-16			
P,X	AU,A, 46046/93 (WIMMERA INDUSTRIAL MINERALS PTY LTD) 18 November 1993 (18.11.93) Example 9	1,2,4,13-16			
P,X	AU,A, 44589/93 (WIMMERA INDUSTRIAL MINERALS PTY LTD) 11 November 1993 (11.11.93) Example 9	1,2,4,13-16			
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex. </div>					
<table style="width: 100%; border: none;"> <tr> <td style="width: 33%; vertical-align: top;"> * Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 33%; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> <td style="width: 33%;"></td> </tr> </table>			* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family				
Date of the actual completion of the international search 18 November 1993 (18.11.93)	Date of mailing of the international search report 23 NOV 1993 (22.11.93)				
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929	Authorized officer <div style="text-align: center; margin-top: 10px;">  VIVIENNE THOM </div> Telephone No. (06) 2832158				

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 93/00414

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	AU,A, 74507/91 (WIMMERA INDUSTRIAL MINERALS PTY LTD) 5 September 1991 (05.09.91) Page 4 lines 17-34, page 8 line 31 - page 9 line 4	
X	US,A, 2815272 (ARMANT et al) 3 December 1957 (03.12.57) Claim 1	1,14-16
A	AU,A, 14981/92 (RGC MINERAL SANDS LIMITED) 22 September 1992 (22.10.92) Claim 1	1-4,14-16

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

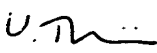
Patent Document Cited in Search Report		Patent Family Member					
AU	70976/87	BR	8701481	EP	243725	ZA	8702399
AU	74507/91	BR	9106105	CA	2077441	EP	517786
		NZ	237273	WO	9113180	ZA	9101515
AU	14981/92	BR	9201442	JP	5180989		
END OF ANNEX							

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 93/00414

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl. ⁵ C22B 1/00, 1/02 // C22B 34/12 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC : C22B 1/00, 1/02, 34/12, 53/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched AU : IPC as above Electronic data base consulted during the international search (name of data base, and where practicable, search terms used)				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.		
X	AU,A, 70976/87 (E.I. DU PONT DE NEMOURS & CO) 8 October 1987 (08.10.87) Page 2 line 25 - page 3 line 10, page 8 line 7 - page 10 line 13	1-4,13-16		
P,X	AU,A, 46046/93 (WIMMERA INDUSTRIAL MINERALS PTY LTD) 18 November 1993 (18.11.93) Example 9	1,2,4,13-16		
P,X	AU,A, 44589/93 (WIMMERA INDUSTRIAL MINERALS PTY LTD) 11 November 1993 (11.11.93) Example 9	1,2,4,13-16		
<div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div> <input checked="" type="checkbox"/> See patent family annex. </div> </div>				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>			
Date of the actual completion of the international search 18 November 1993 (18.11.93)		Date of mailing of the international search report 23 NOV 1993 (22.11.93)		
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. 06 2853929		Authorized officer  VIVIENNE THOM Telephone No. (06) 2832158		

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate of the relevant passages	Relevant to Claim No.
X	AU,A, 74507/91 (WIMMERA INDUSTRIAL MINERALS PTY LTD) 5 September 1991 (05.09.91) Page 4 lines 17-34, page 8 line 31 - page 9 line 4	1,14-16
X	US,A, 2815272 (ARMANT et al) 3 December 1957 (03.12.57) Claim 1	1-4,14-16
A	AU,A, 14981/92 (RGC MINERAL SANDS LIMITED) 22 September 1992 (22.10.92) Claim 1	

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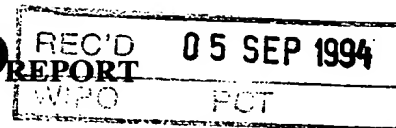
Patent Document Cited in Search Report		Patent Family Member					
AU	70976/87	BR	8701481	EP	243725	ZA	8702399
AU	74507/91	BR	9106105	CA	2077441	EP	517786
		NZ	237273	WO	9113180	ZA	9101515
AU	14981/92	BR	9201442	JP	5180989		
END OF ANNEX							

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32

PATENT COOPERATION TREATY
PCT
INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rules 70)



Applicant's or agents file reference GRM:R:FP2155	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International application No. PCT/AU 93/00414	International filing date 12 August 1993 (12.08.93)	Priority Date 14 August 1992 (14.08.92)
International Patent Classification (IPC) or national classification and IPC Int. Cl. 5 C22B 1/00, 1/02 // C22B 34/12		
Applicant (1) TECHNOLOGICAL RESOURCES PTY LTD (2) HOLLITT, Michael John et al.		

1.	This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2.	This REPORT consists of a total of 4 sheets, including this cover sheet. <input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheet of description, claim and/or drawings amended during international preliminary examination and/or containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of sheets.
3.	This report contains indications relating to the following items: I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input checked="" type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application

Date of submission of the demand 15 March 1994 (15.03.94)	Date of completion of this report 24 August 1994 (24.08.94)
Name and mailing address of the IPEA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No. (06) 2853929	Authorized officer J.P. ELJAH Telephone No. (06) 2832161

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I. Basis of the report

1. This report has been drawn on the basis of *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:



the international application as originally filed.



the description,

pages ..., as originally filed,
pages ..., as filed with the demand,
pages ..., filed with the letter of ...,
pages ..., filed with the letter of ...,



the claims,

Nos. ..., as originally filed,
Nos. ..., as amended under Article 19,
Nos. ..., filed with the demand,
Nos. ..., filed with the letter of ...,
Nos. ..., filed with the letter of ... ,



the drawings,

sheets/fig ..., as originally filed,
sheets/fig ..., filed with the demand,
sheets/fig ..., filed with the letter of ...,
sheets/fig ..., filed with the letter of ... ,

2. The amendments have resulted in the cancellation of:



the description, pages ...



the claims, Nos. ...



the drawings, sheets/fig ...

3.



This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

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V. Reasoned statement under Article 35(2) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement**1. STATEMENT**

Novelty (N)	Claims 1-16	YES
	Claims	NO
Inventive Step (IS)	Claims 1-16	YES
	Claims	NO
Industrial Applicability (IA)	Claims 1-16	YES
	Claims	NO

2. Citations and explanations

AU,A, 70976/87 (E.I. DU PONT DE NEMOURS & CO) 8 October 1987 (08.10.87)

AU,A, 74507/91 (WIMMERA INDUSTRIAL MINERALS PTY LTD) 5 September 1991 (05.09.91)

US,A, 2815272 (ARMANT et al) 3 December 1957 (03.12.57)

The above citations do not disclose the formation of a solid titaniferous phase and a liquid oxide or glassy phase during the heating of a titaniferous material.

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VI. Certain documents cited

1. Certain published documents (Rule 70.10)

Application No. Patent No.	Publication date (day/month/year)	Filing date (day/month/year)	Priority date (valid claim) (day/month/year)
AU,A, 44589/93	11 November 1993 (11.11.93)	12 August 1993 (12.08.93)	2 March 1990 (02.03.90)
AU,A, 46046/93	18 November 1993 (18.11.93)	2 September 1993 (02.09.93)	2 March 1990 (02.03.90)

2. Non-written disclosures (Rule 70.9)

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